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ON-LINE MEASUREMENT OF THE INFRARED SPECTRA OF GAS CHROMATOGRAPHIC ELUENTS

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact and control of specific environmental contaminants, the Analytical Chemistry Branch develops techniques for identifying and measuring chemical pollutants in water and soil.

This report described the development of two systems for improving detection limits for gas chromatography - Fourier Transform infrared spectroscopy (GC-FTIR). GC-FTIR is being evaluated by EPA for applic ations in identifying organic pollutants at trace concentrations in water. If the technique proves feasible, it will improve the assessment of health and ecological effects of organic compounds in water and improve the development and implementation of control measures.

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ABSTRACT

Techniques for increasing the sensitivity of the interface between a gas chromatograph and a rapid-scanning Fourier transform infrared spectrometer (GC-IR) have been developed. A single-beam system, in which a triglycine sulfate (TGS) detector is used to measure the interferogram, has been designed and constructed. Identifiable infrared spectra of submicrogram quantities eluting from a gas chromatograph have been measured without trapping the sample using this system. A double-beam configuration for GC-IR has also been designed so that a cooled mercury cadmium telluride detector can be used to further decrease the detection limits without limiting the sensitivity by digitization noise. Each of these systems necessitates the use of light-pipes with relatively long (30 cm) absorbing paths but low reflection losses.

This report was submitted in fulfillment of Grant Number R803517-01-0 by Ohio University under the (partial) sponsorship of the U.S. Environmental Protection Agency. Work on the task of further increasing the sensitivity of the GC-IR interface is continuing under E.P.A. Grant R804333-01-0. This report covers the period from 1/20/75 to 1/19/76 and work was completed as of 1/19/76.

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ABBREVIATIONS

DB-FT-IR	-- dual-beam Fourier transform infrared spectroscopy
FT-IR	-- Fourier transform infrared spectroscopy
GC	-- gas chromatography
GC-IR	-- the interface between a gas chromatograph and a rapid-scanning infrared spectrometer for the on-line measurement of the infrared spectra of components of mixtures separated by gas chromatography
GC-MS	-- the interface between a gas chromatograph and a mass spectrometer for the on-line measurement of the mass spectra of components of mixtures separated by gas chromatography
MCT detector	-- mercury cadmium telluride photoconductive infrared detector
µg	-- microgram, 10^{-6} grams
ng	-- nanogram, 10^{-9} grams
SCOT columns	-- support-coated open tubular columns for gas chromatography
TGS detector	-- triglycine sulfate pyroelectric infrared detector
D*	-- figure of merit for detector sensitivity

SECTION I

INTRODUCTION

Before this project was initiated, the most sensitive interface between a gas chromatograph and an infrared spectrometer (GC-IR) designed for use with a commercial Fourier transform infrared (FT-IR) spectrometer was an accessory to the Model FTS-14 spectrometer marketed by Digilab Inc. (Cambridge, MA). The detection limits for "on-the-fly" measurements of the infrared spectra of most materials eluting from a gas chromatograph that were determined using this accessory were not very low, typically 3 to 20 micrograms (μg); for most analytical purposes, submicrogram sensitivity is desirable. It has been shown (1) that the light-pipe used in the Digilab GC-IR accessory is too short (5 cm in length) and too wide (6 mm in diameter) to permit the optimum GC-IR sensitivity to be achieved. The same calculations showed that a longer, narrower light-pipe would give increased sensitivity by providing a substantially increased optical path without seriously attenuating the radiation by reflection losses. A light-pipe of approximately the optimum dimensions for GC-IR (300 x 4 x 4 mm) is sold by Norcon Instruments Inc. (S. Norwalk, CT), and the first phase of this project involved interfacing this light-pipe to an FTS-14 spectrometer.

A different source from the nichrome wire source used on the FTS-14 spectrometer was also proposed for use with this GC-IR system. Nichrome wire sources may not be operated regularly at a temperature much above dull red heat, since at higher temperatures their lifetime is much reduced. The decision was made to use a Nernst glower, since sources of this type operate at the highest temperatures of all common infrared sources.

SECTION II

CONCLUSIONS

A sensitive interface between a gas chromatograph and a rapid scanning Fourier transform infrared spectrometer was developed. The improved sensitivity was derived by modifications on the standard Digilab FTS-14 Fourier transform spectrometer, viz.

(i) replacement of the existing nichrome wire sources of the FTS-14 with a modified Nernst glower source to permit operation at higher temperatures than is possible with nichrome wire;

(ii) installation of a light-pipe gas-cell of dimensions 300 x 4 x 4 mm using two specially designed aspherical mirrors to focus the beam into the light-pipe and refocus the beam emerging from the light-pipe onto a 2 mm square detector.

With these modifications, identifiable spectra from submicrogram quantities of strong infrared absorbers could be obtained without trapping the sample.

When the triglycine sulfate (TGS) detector being used for the measurement was replaced by an MCT detector, some improvement in GC-IR sensitivity was demonstrated, but the principal limitation to the sensitivity of the system changed from detector noise to digitization noise.

Longer and narrower light-pipes are needed for single beam GC-IR measurements using the sensitive MCT detectors to circumment digitization noise limitations. Since work along this line had been under intensive investigation at the U. S. Environmental Protection Agency's laboratory at Athens, Georgia, it was not pursued further in this project although it constituted the second part of the proposal.

Feasibility studies showed that the dual beam Fourier transform infrared (DB-FT-IR) technique is uniquely suited for the elimination of digitization noise problems that are found in FT-IR when a sensitive detector is used for the measurement of absorption spectra with an optically efficient sampling configuration. It is fundamentally a different approach and holds promise for further improvement of the sensitivity of the GC-IR interface. A complete optical system for GC-IR using this technique was designed and is currently being built.

SECTION III

RECOMMENDATIONS

The experimental part of this project was largely limited to the relatively low sensitivity single-beam method for GC-IR. Substantially increased sensitivity should be achieved through the use of dual-beam Fourier transform infrared spectroscopy. With this method using light-pipes of similar dimensions to the ones used in the single-beam experiment, it is possible to utilize a liquid nitrogen cooled mercury cadmium telluride detector without limiting the sensitivity of GC-IR by digitization noise. It is recommended that such a system should be constructed and tested.

One potential method of improving the automation and, to a lesser extent, the sensitivity of GC-IR is the development of an efficient trigger to initiate and terminate data collection.

It should also be noted that if the concentration of the analyte in any GC peak could be increased, for example in the same fashion as sample concentrators for the interface between a gas chromatograph and a mass spectrometer (GC-MS), a further increase in GC-IR sensitivity, by as much as a factor of four, could be obtained.

SECTION IV

EXPERIMENTAL

An optical bench was constructed with the following components.

Source. A modified Nernst glower (137 type source from Perkin-Elmer Corporation, Norwalk, CT) was used. The resistance of this source is very low at ambient temperature so that the source could not be heated directly using any d.c. power supply available for this project, since the current required to heat the source caused an overload for the power supply. To get around this problem the source was initially heated by a.c. (using a Variac to control the voltage). After the source had reached red heat, a 6 v.d.c. power supply (Lambda Electronics, Melville, N.Y.) was switched on in place of the a.c. supply. A 3" focal length 45° off-axis paraboloidal mirror (Special Optics, Little Falls, N.J.) was used to collect the radiation emitted by this source and produce an approximately collimated beam of radiation 2" in diameter as input into the interferometer. Both the source and the collimating mirror were mounted on a baseplate which butted directly up against the interferometer.

Interferometer. A standard Digilab Model 296 Michelson interferometer was used. The optical bench was kept close to the optical head of the FTS-14 spectrometer (from which the interferometer had been removed), and the position of the electronic controller was not changed. The cables from the controller to the interferometer were long enough that no extension cabling was necessary for the system to be used in this configuration.

Focusing Paraboloid. The exit beam from the interferometer was brought to a 3-mm diameter focus using an identical off-axis paraboloid to the one mounted in the source unit. The entrance to the light-pipe was at this focus.

Light-pipe and oven. A Norcon Instrument light-pipe and oven assembly was used. The light-pipes were 30 cm long and square (4-mm side) in cross-section. These light-pipes were constructed using four identical rectangular strips of glass with one side gold-coated. They were mounted in an oven, the maximum temperature of which was 250°C. Only one of the two light-pipes in this assembly was used in the first phase of this project. The effluent gas from the gas chromatograph was passed down a flexible heated tube (Wilks Scientific Corporation, S. Norwalk, CT) to the light-pipe. All exposed surfaces of the delivery system were heated and wrapped in asbestos tape. The temperature was monitored at several points to ensure no cold-spots were present.

Focusing ellipsoid. The beam emerging from the light-pipe was focused onto the detector using a 45° off-axis section of an ellipsoidal mirror whose two focal lengths were 1.6" and 5.6". The diameter of the refocused beam was 2-mm.

Detector. A 2-mm square triglycine sulfate (TGS) detector was generally used for the measurements. This detector could be replaced by an MCT detector, the element of which was also 2-mm square.

With these optics the transmittance between the interferometer and the detector was 20% to 25% enabling low noise spectra to be measured using a TGS detector with just a few seconds measurement time.

The typical experimental procedure was as follows. The effluent from the gas chromatograph was monitored using a thermal conductivity detector and passed through the light-pipe continuously (via the heated transfer line). Interferograms were signal-averaged during the time that each peak was present in the light-pipe, and interferograms from successive GC peaks were stored in sequential arrays in the data system of the spectrometer. At the end of the chromatogram, each interferogram was recalled and transformed (generally using double-precision software), and the resulting single-beam spectrum was ratioed against a stored low-noise background spectrum of the empty cell. The resulting ratio-recorded spectrum could be output in a linear transmittance or linear absorbance format.

SECTION V

RESULTS

Early calculations (1) showed that the minimum amount of a strongly absorbing material (e.g. salicylaldehyde) from which a recognizable spectrum (i.e. at least five bands with a signal-to-noise ratio greater than 2:1) could be obtained with this system was approximately 800 nanograms (ng). Figure 1 shows that this estimate was quite accurate.

It was found that the use of a Nernst glower source allowed spectra to be measured at about twice the sensitivity attainable with a nichrome wire source below 2000 cm^{-1}. However above 2000 cm^{-1} the emissivity of the Nernst glower falls off quite rapidly; and in spite of the fact that the Nernst glower can be operated at a higher temperature than the nichrome wire source, the spectral energy density of this source is actually slightly lower than that of the nichrome wire about 3000 cm^{-1}. Thus the noise-level of transmittance spectra was substantially lower (by about a factor of five) in the fingerprint region of the spectrum, below 2000 cm^{-1}, than in the C-H and O-H stretching region between 3800 and 2800 cm^{-1}.

The feasibility of using an MCT detector with this optical arrangement was also studied. In order to avoid "clipping" the interferogram (2), it was found that the source had to be operated below red heat. Even under these far from optimum conditions, a recognizable spectrum of approximately 200 ng of salicylaldehyde could be obtained below 2000 cm^{-1}. Since the response of the MCT detector falls off above 2000 cm^{-1} and because the temperature of the source was so low, the noise around 3000 cm^{-1} in ratio-recorded spectra was very high.

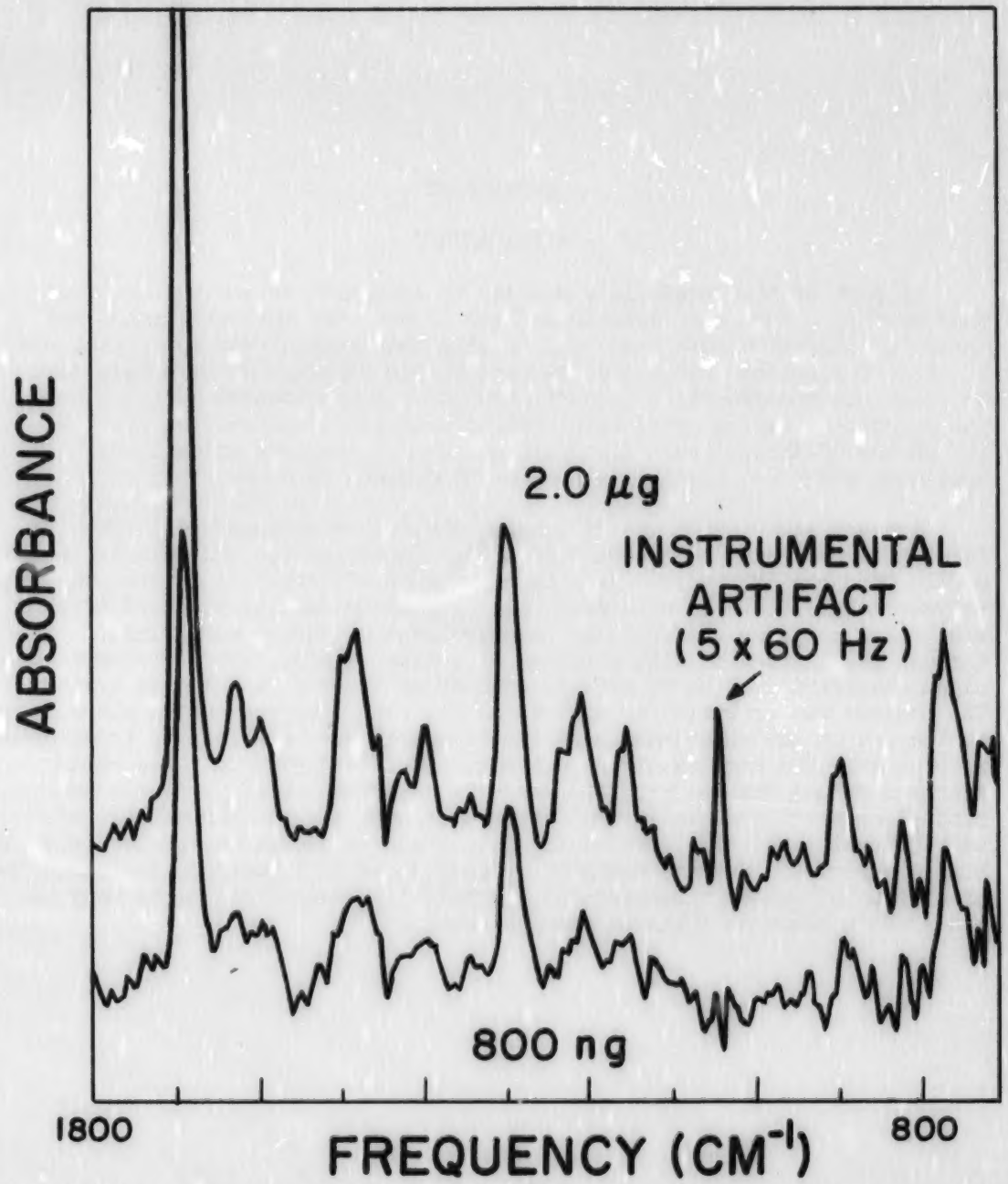

Figure 1. On-line GC-IR spectrum of 2 μg and 800 ng of salicylaldehyde measured using a TGS detector.

SECTION VI

APPLICATIONS

As part of the feasibility studies to determine detection limits of this system, a series of chlorinated pesticides was chromatographed and their GC-IR spectra were measured. During this work it was found that one of these pesticides, Endrin, decomposed on the column. We have been able to study the decomposition products and go some way towards determining the reaction kinetics by applying scaled absorbance subtraction routines (3) on the GC-IR spectra. This work is not yet complete and will be continued after the funding period for this grant is over.

Another study which was made using the system constructed in the first phase of this project concerned the identification and quantification of the products of the pyrolysis or combustion of certain polymers and polymer composites. In this work (4) the gaseous species produced after a small (1-2 mg) sample of polymer was pyrolyzed or burned were flushed through the light-pipe with a stream of helium or air. Interferograms were signal-averaged over short periods of time and stored in the data system. The process was repeated for as long as the pyrolysis was taking place, and at the end of the experiment each interferogram was recalled and transformed in precisely the same manner as a typical GC-IR experiment. This rapid infrared method for studying the products and kinetics of pyrolysis and combustion reactions has several advantages over the gas chromatographic methods used previously, especially when reactive inorganic species (such as HCl) are formed. Whereas using GC methods it is only possible to follow the production of two or three species, by this infrared technique as many as ten species could be followed simultaneously.

SECTION VII

DISCUSSION AND FUTURE WORK

The second part of the proposal for this project was for a study of the effect of using longer, narrower light-pipes than the Norcon light-pipes used in the first phase of the project. In this case, the absorbing path would be increased but reflection losses would decrease the overall transmittance of the system. When the transmittance of the system is reduced below about 10%, an MCT detector can be used without running into the problems of digitization noise (5). However before this phase of the project was started, Azarraga (6) had already made a study of the feasibility of using optics of this type. His results showed detection limits close to those predicted in the proposal for this project. It was therefore believed that there was no point in repeating this approach, and work was started on another method for further increasing the sensitivity of GC-IR measurements. This system involved the use of dual-beam Fourier transform infrared (DB-FT-IR) techniques. To recognize the reasons for adopting this approach, the limitations of current GC-IR systems will first be discussed.

The system developed in the first phase of this project probably came within a factor of two from meeting the lowest detection limits possible with a state-of-the-art FT-IR spectrometer and a TGS detector. The light-pipe provided a fairly long absorbing path without seriously attenuating the beam due to reflection losses. Therefore a fairly high proportion of the energy leaving the interferometer reaches the detector. If an MCT detector is interfaced to this system with the source at its maximum temperature, the interferogram would become digitization noise limited, so that the increase in sensitivity gained through the use of a more sensitive detector is less than the ratio of the D*'s of the two detectors. By using longer, narrower light-pipes the energy reaching the detector may be attenuated to the point that an MCT detector can be used without the problem of digitization noise.

If one could use an MCT detector with light-pipes of high transmittance but <u>without</u> encountering the problems of digitization noise, it is apparent that a further increase in GC-IR sensitivity could be achieved. The application of DB-FT-IR techniques should allow this goal to be realized. In DB-FT-IR (7), use is made of the fact that the two beams emerging from an interferometer are exactly 180° out-of-phase. For an ideal interferometer, if these two complementary beams traverse optically identical paths and are passed onto the same detector, no net a.c. interferogram would result. If a sample of low absorbance is present in one beam and not the other, the interferogram is due solely to the sample absorption bands, and the smaller is the quantity of sample present in the beam, the smaller is the interferogram. (This is, of course, the reverse of the more conventional

single-beam FT-IR methods, where the smaller the amount of sample in the beam, the greater is the intensity of the interferogram). Thus for DB-FT-IR, a sensitive detector can be used to measure the spectra of samples at low concentration using an MCT detector without encountering the problems of digitization noise.

The final phase of this project was spent designing a dual-beam optical system for GC-IR using the high transmittance Norcon light-pipes used in the first phase of this study. In our final design, see Figure 2, the input beam to the interferometer is slightly skewed, so that both output beams can be collected and passed through the two parallel light-pipes in the Norcon oven assembly. The beams emerging from the light-pipes are then focused on a single MCT detector. After this system was designed, all components and mirrors were ordered well before the completion date for this project. However delays in the delivery of the two off-axis ellipsoidal mirrors required to focus the two beams onto the detector have meant that we have not yet been able to construct and test this system.

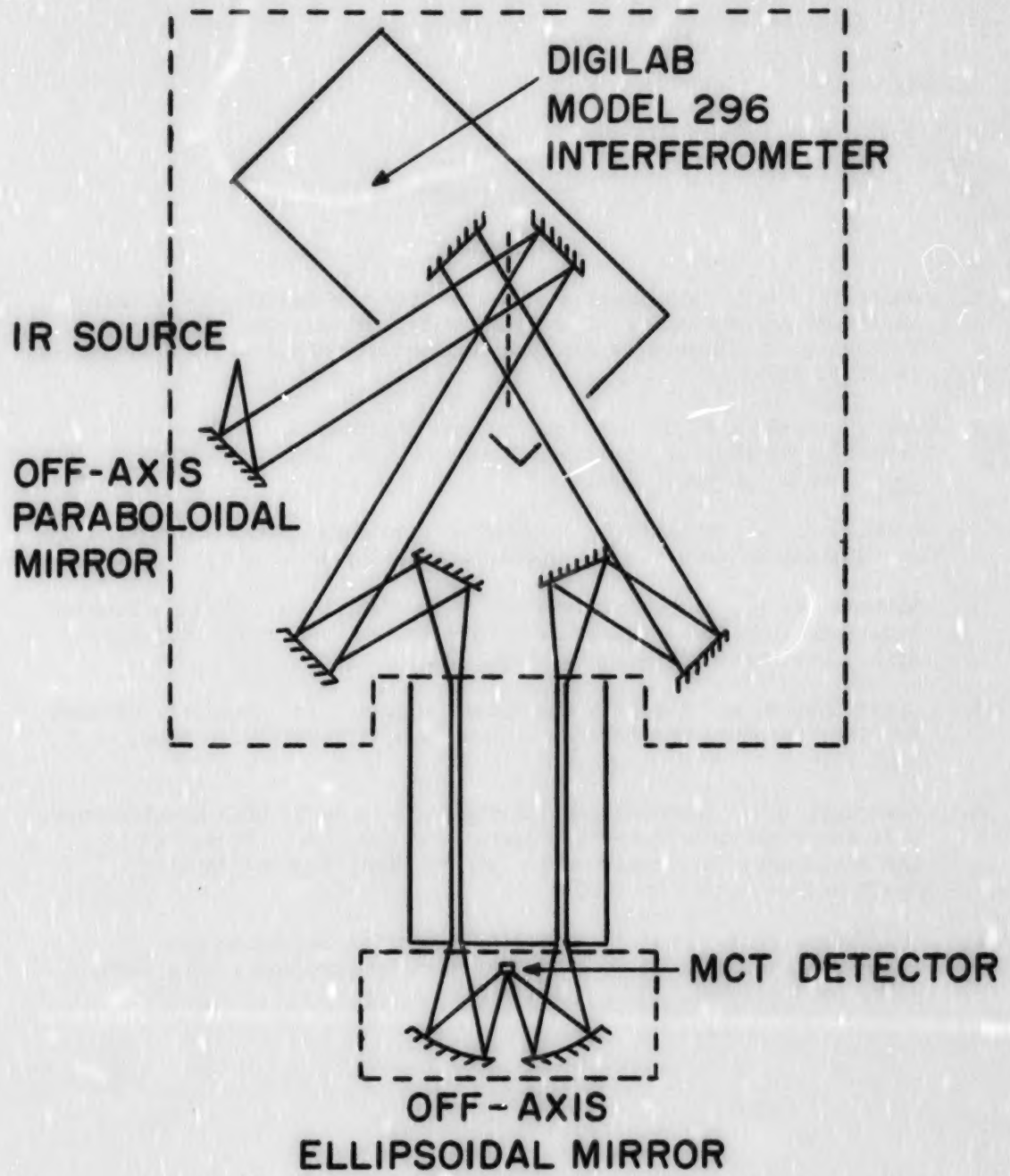

Figure 2. Dual-beam FT-IR optical configuration for high sensitivity GC-IR.

SECTION VIII

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